

# Chemistry

## Lecture 4

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### Alcohols, Phenols, Ethers

#### Outline:

#### Alcohols:

- ✚ Classification
- ✚ Nomenclature
- ✚ Reactivity

#### Phenols:

- ✚ Physical properties
- ✚ Nomenclature
- ✚ Acidity
- ✚ Reactivity

### Alcohols

- General formula is  $C_nH_{2n+2}O$  or  $C_nH_{2n+1}OH$

#### Types:

- ◆ **Monohydric Alcohols:** Alcohols having only one –OH group
- ◆ **Dihydric Alcohols:** Alcohols having two –OH group
- ◆ **Polyhydric Alcohols:** Alcohols having more than two –OH group

#### Types of Monohydric Alcohols:

- ◆ **Primary Alcohols:** If carbon to which –OH group is attached is further directly attached with one or no carbon atom.
- ◆ **Secondary Alcohols:** If carbon to which –OH group is attached is further directly attached with two carbon atoms.
- ◆ **Tertiary Alcohols:** If carbon to which –OH group is attached is further directly attached with three carbon atoms.

#### Common Names of Alcohols:

- ◆ Alkyl alcohol  
like  $CH_3OH$  is methyl alcohol,  $C_2H_5OH$  is called ethyl alcohol

## IUPAC Rules for Alcohols:

### Selection of Chain:

- ◆ Select the longest continuous carbon chain to –OH group is attached directly.
- ◆ If more than one chain is of same length, then select one with maximum no. of –OH groups.
- ◆ If no. –OH groups is same, select one with maximum substituents and if substituents are also same, then select any.

### Numbering:

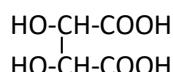
- ◆ Start numbering from the end nearer to –OH group and if –OH group is at same distance from both ends, start numbering from end nearer to substituent.
- ◆ If substituent is also at same distance, then start numbering from either end.

### Naming:

- ◆ Name alkane is replaced with “alkanol”.
- Position of substituent-name of substituent-position of OH group-alkanol
- ◆ If more than one -OH groups are present, use diol, triol, tetraol etc.

(OH)CH2-CH-CH2-CH(OH)-CH3 (1,4-Pentadiol or Pent-1,4-diol)

- ◆ In case of unsaturated alcohols, -OH group is preferred over double or triple bonds.  
CH2=CH-CH2-CH2OH  
3-Buten-1-ol or But-3-en-1-ol
- ◆ If more than functional groups are present, preference is with one coming first in priority list i.e.



2,3-Dihydroxy butane-1,4-dioic acid (Tartaric acid)



2-Hydroxy propanoic acid (Lactic acid)

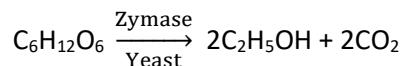
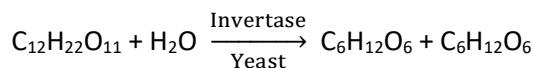
## Preparation of Ethanol

- ◆ By Fermentation (a biochemical process occurs in presence of enzymes)
- ◆ Necessary condition are:
  - ❖ Optimum temperature (25-35°C)
  - ❖ Proper aeration
  - ❖ Dilution of solution
  - ❖ Absence of any preservative
- ◆ In Pakistan prepared from **molasses, starch, grains, and fruit juices.**

### From Molasses:

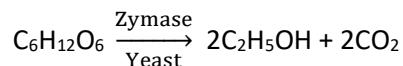
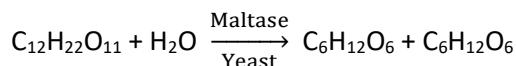
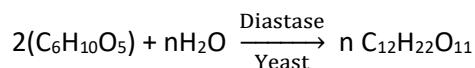
- Residue after crystallization of sugar from sugar juice

- So it is sucrose
- Sucrose on hydrolysis in presence of Invertase breaks into glucose and fructose
- Glucose further decomposes in presence of Zymase to give ethanol



### From Starch:

- Starch on hydrolysis in presence of Diastase breaks into maltose
- Maltose on hydrolysis in presence of Maltase breaks into glucose units
- Glucose further decomposes in presence of Zymase to give ethanol



- ◆ Ethanol never exceeds 12-14 % as beyond this limit enzyme becomes inactive
- ◆ Distillation gives Rectified spirit (95 %)
- ◆ Distillation in presence of CaO gives Absolute alcohol (100 %)
- ◆ 10 % methanol is added in ethanol to avoid its drinking (denaturing)
- ◆ Pyridine or acetone can be used

### Reactions of Alcohol

1. When O-H bond to is be broken	2. When C-O bond is to be broken
Act as nucleophile except as acid with only Na	Act as electrophile
Attack of electrophile on it	Attack of nucleophile on it
Show electrophilic substitution reactions except with Na gives acid base reaction	Show nucleophilic substitution reactions
Reactivity/Acidity; <b>Methyl alcohol &gt; 1° &gt; 2° &gt; 3°</b>	Reactivity; <b>3° &gt; 2° &gt; 1° &gt; Methyl alcohol</b>
$2\text{C}_2\text{H}_5\text{OH} + 2\text{Na} \xrightarrow{\text{Ether}} 2\text{C}_2\text{H}_5\text{ONa} + \text{H}_2$	$\text{C}_2\text{H}_5\text{OH} + \text{SOCl}_2 \xrightarrow{\text{Pyridine}} \text{C}_2\text{H}_5\text{Cl} + \text{SO}_2 + \text{HCl}$
$\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{MgI} \xrightarrow{\text{ZnCl}_2} \text{CH}_4 + \text{Mg}(\text{I})(\text{OC}_2\text{H}_5)$	$\text{C}_2\text{H}_5\text{OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O}$
$\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} \xrightleftharpoons{\text{H}_2\text{SO}_4} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$	$\text{C}_2\text{H}_5\text{OH} + \text{NH}_3 \xrightarrow{\text{ThO}_2} \text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O}$ $\text{C}_2\text{H}_5\text{OH} + \text{PCl}_3 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{H}_3\text{PO}_3$ $\text{C}_2\text{H}_5\text{OH} + \text{PCl}_5 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{POCl}_3 + \text{HCl}$

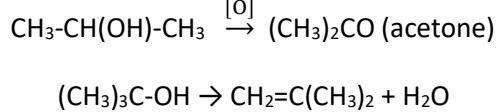
The rate of esterification of alcohol is more for?  
 C<sub>2</sub>H<sub>5</sub>OH CH<sub>3</sub>OH (CH<sub>3</sub>)<sub>2</sub>CHOH (CH<sub>3</sub>)<sub>3</sub>COH

### 3. Oxidation Reactions:

- $\text{KMnO}_4/\text{H}_2\text{SO}_4 \Rightarrow$  Pink colour of  $\text{KMnO}_4$  disappears
- $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4 \Rightarrow$  Colour turns green due to reduction of dichromate ion ( $\text{Cr}^{+6}$ ) to chromate ion ( $\text{Cr}^{+3}$ )
- Primary alcohols on oxidation give aldehydes which in same conditions further oxidize to carboxylic acids.
- Secondary alcohols on oxidation give ketones which do not oxidize further in such conditions
- Tertiary alcohols don't oxidize rather undergo elimination reaction to give alkene

Which of the following alcohol not undergo oxidation?

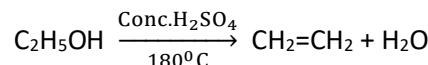
ethanol propanol iso-butanol  
2-methyl-2-propanol



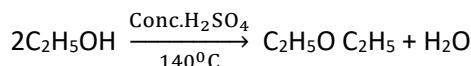
Oxidation of iso-propyl alcohol yields?

propane propanone propanal  
propanoic acid

### 4. Dehydration:



The dehydration of alcohol results in:  
alkene aldehyde ether both a, c



### 5. Lucas Test:

- Alcohols form oily layer of respective alkyl halide with  $\text{HCl}$  in presence of  $\text{ZnCl}_2$
- Primary alcohols form oily layer on heating
- Secondary alcohols form oily layer in 5-10 min.
- Tertiary alcohols form oily layer immediately

### 6. Iodoform Test ( $\text{I}_2/\text{NaOH}$ ):

What happens when iodine is treated with methyl alcohol in presence of base?  
Oily layer forms yellow ppt form no reaction

- Yellow ppts. of iodoform ( $\text{CHI}_3$ ) forms
- Only ethanol gives iodoform test among primary alcohols
- Those secondary alcohols give iodoform test in which at least one  $-\text{CH}_3$  group is attached with  $\alpha$ -carbon
- Tertiary alcohols don't give iodoform test

### Uses of Methanol

- Methanol is used as a solvent for fats oils, paints, and varnishes.
- It is also used as antifreeze in the radiators of automobiles
- For denaturing of alcohol.

## Uses of Ethanol

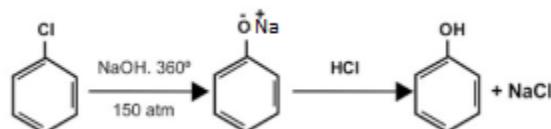
- Ethanol is used as a solvent, as a drink and as a fuel in some countries.
- It is used in pharmaceutical preparations
- As a preservative for biological specimen.

## Phenol

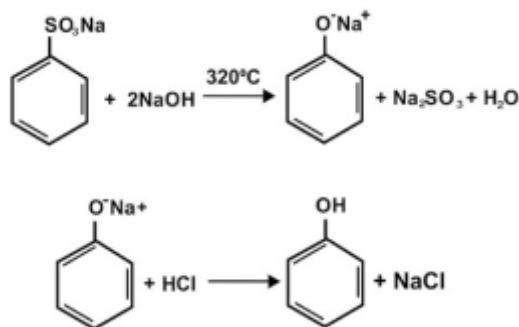
- Carbolic acid
- Obtained from coal tar by Runge
- Deliquescent
- Anesthetic
- Sparingly soluble in water at room temp. giving pink solution.
- Poisonous with characteristic phenolic order
- Used to prepare pharmaceutical drugs
- As disinfectant in hospitals and washrooms
- More acidic than alcohol and water due to stability of phenoxide ion
- Phenoxide ion has 5 resonating structures (reason for stability)
- Acidity order   **Carboxylic acid > Phenol > Water > Alcohol**

## Preparation of Phenol

### ➤ From Chlorobenzene (Dow's method)



### ➤ From sodium salt of benzene sulphonic acid



## Reactions of Phenol

### (a) Involving Benzene Ring:

#### ◆ With Br<sub>2</sub>:

- Test to distinguish phenol from rest



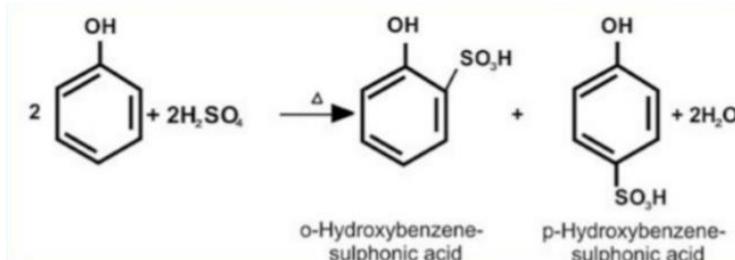
- White ppts. of 2,4,6-Tribromophenol

◆ Nitration:



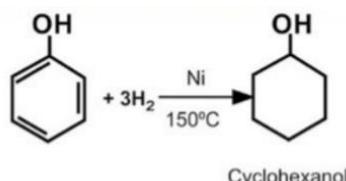
◆ Sulphonation:

- Phenol reacts with conc.  $\text{H}_2\text{SO}_4$  to form ortho, para hydroxy benzene sulphonic acid.



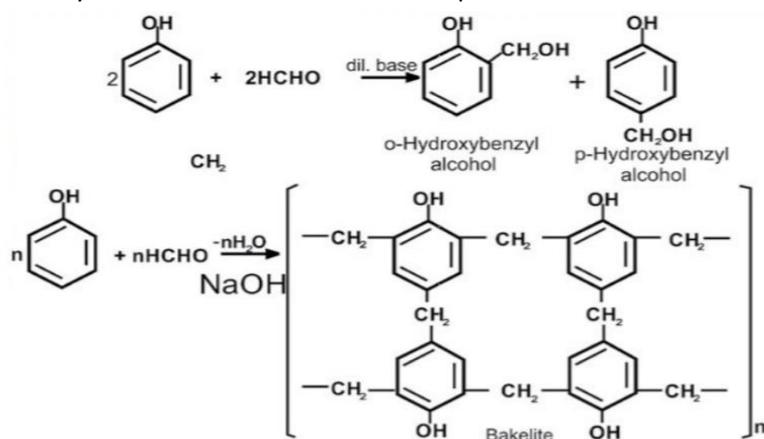
◆ Hydrogenation:

- On hydrogenation, phenol gives cyclohexanol



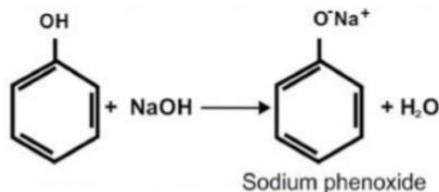
◆ Reaction with Formaldehyde:

- Phenol + formaldehyde in presence of alkali/acid produce ortho, para hydroxyl benzyl alcohol
- This hydroxyl benzyl alcohol further react with phenol molecule to form Bakelite (polymer).

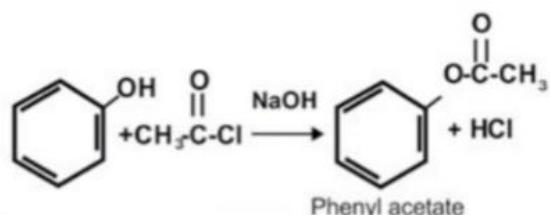


**(b) Involving –OH group:**

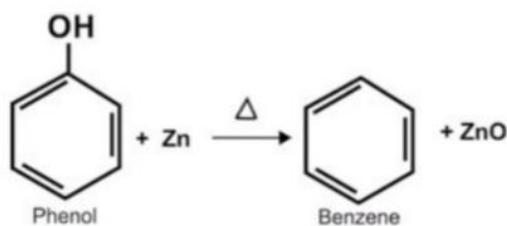
- ◆ **Salt Formation:** Phenol reacts with alkalies to form salts



- ◆ **Ester Formation:** Phenol reacts with acetyl chloride in presence of base to form ester



- ◆ **Reduction with Zn:** Phenol reduces with Zn to give benzene



## Ethers

**Common Names of Ethers:**

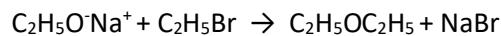
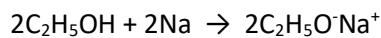
- ✿ If R groups are same, use di as prefix i.e. CH<sub>3</sub>-O-CH<sub>3</sub> is Dimethyl ether.
- ✿ If R groups are different, name them alphabetically i.e C<sub>2</sub>H<sub>5</sub>-O-CH<sub>3</sub> is Ethyl methyl ether.

**IUPAC Names of Ethers:**

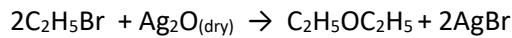
- ✿ If R groups are different, name the smaller R group as “**alkoxy**” while the larger group as parent name “**alkane**”.
- ✿ If R groups are different, name the any of them as “**alkoxy**” while the other one as parent name “**alkane**”.

## Preparation of Ethers

### (a) Williamson synthesis



(b)



## Reactivity

- Comparatively inert
- Behave as lewis base

